

Supporting Information

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Phenylpropanoids, Sesquiterpenoids and Flavonoids from *Pimpinella tragium* Vill. subsp. *lithophila* (Schischkin) Tutin

Hilal Özbek¹, Zühal Güvenalp^{1*}, Ayşe Kuruüzüm-Uz²,

Cavit Kazaz³ and L. Ömür Demirezer²

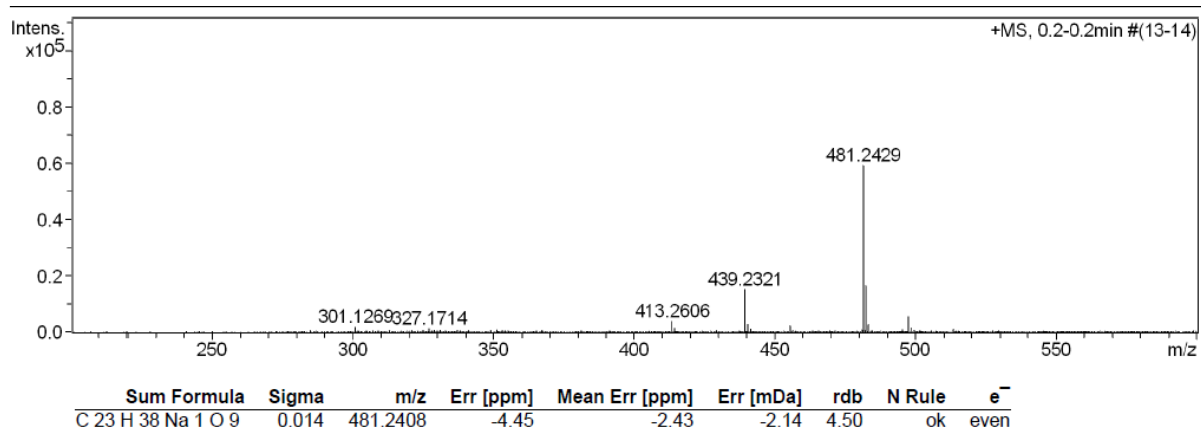
¹*Department of Pharmacognosy, Faculty of Pharmacy, Atatürk University, 25240 Erzurum, Türkiye*

²*Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University, 06100 Ankara, Türkiye*

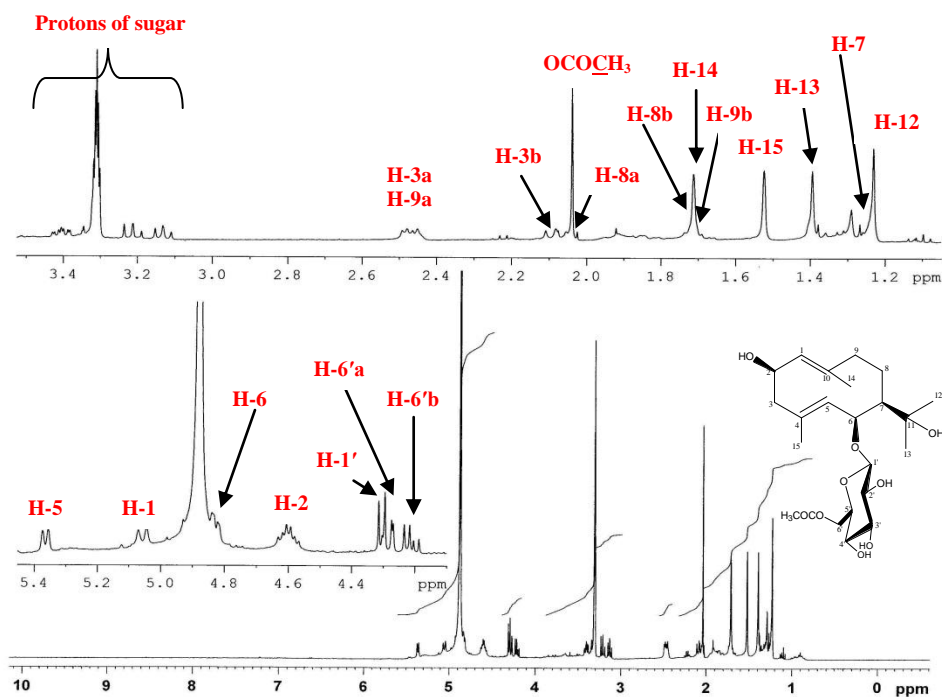
³*Department of Chemistry, Faculty of Science, Atatürk University, Erzurum 25240, Türkiye*

Table of Contents	Page
S1: HR-ESI-MS Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	3
S2: ¹ H-NMR (400 MHz, CD ₃ OD) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	4
S3: ¹³ C-NMR (100 MHz, CD ₃ OD) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	5
S4: DEPT (100 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	6
S5: COSY (400 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	7
S6: COSY Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside) (From 1.0 to 5.5 ppm)	8
S7: HMQC (400 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	9
S8: HMQC (400 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside) (From 10 to 55 ppm)	10

S9: HMQC (400 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside) (From 60 to 85 ppm)	11
S10: HMBC (400 MHz) Spectrum of Compound 1 (Germacradiene-6- <i>O</i> -(6'- <i>O</i> -acetyl)- β -D-glucoside)	12
S11: HR-ESI-MS Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	13
S12: ¹ H-NMR (400 MHz, CD ₃ OD) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	14
S13: ¹³ C-NMR (100 MHz, CD ₃ OD) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	15
S14: DEPT 90 (100 MHz, CD ₃ OD) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	16
S15: DEPT 135 (100 MHz, CD ₃ OD) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	17
S16: COSY (400 MHz) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	18
S17: COSY Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside) (From 3.0 to 8.0 ppm)	19
S18: HMQC (400 MHz) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	20
S19: HMQC (400 MHz) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside) (From 40 to 80 ppm)	21
S20: HMQC (400 MHz) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside) (From 90 to 125 ppm)	22
S21: HMBC (400 MHz) Spectrum of Compound 2 (Rhamnetin-3- <i>O</i> -(2''- <i>O</i> - β -D-glucopyranosyl)- β -D-galactopyranoside)	23

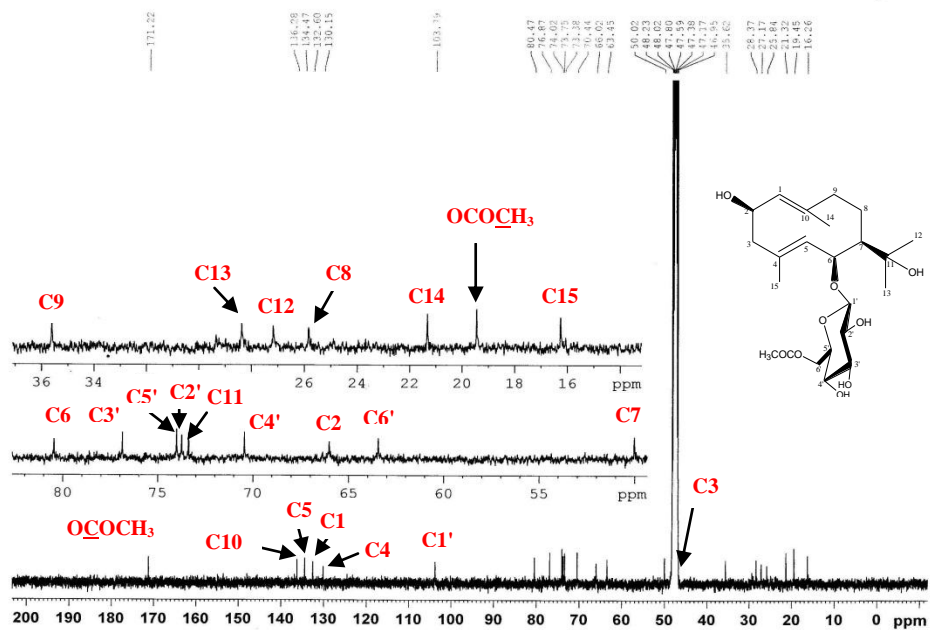


S1: HR-ESI-MS Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)

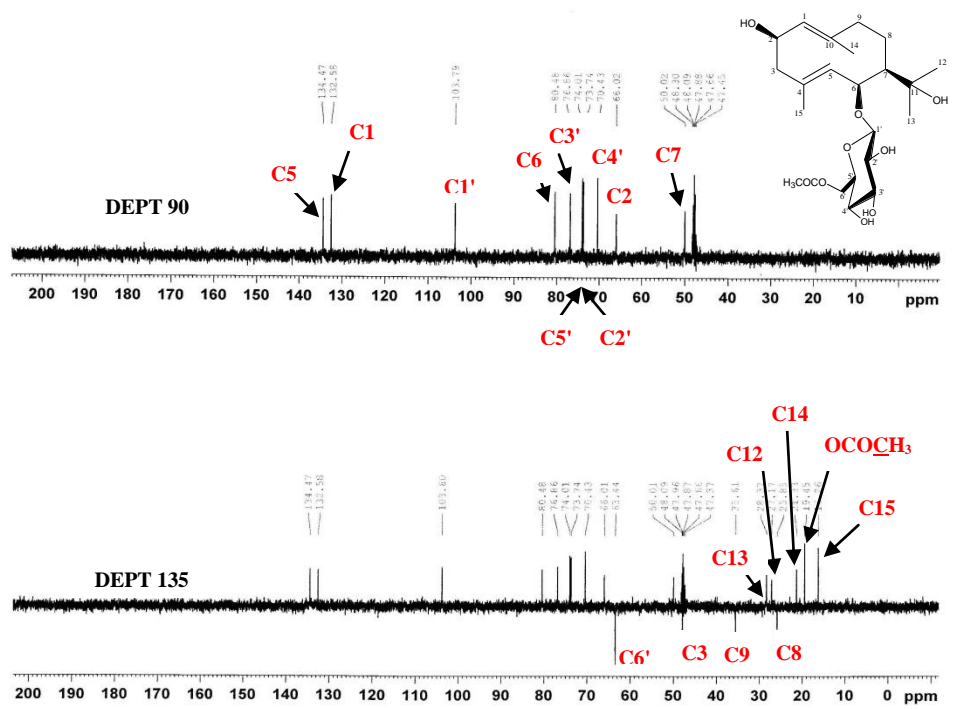


S2: $^1\text{H-NMR}$ (400 MHz, CD_3OD) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -*D*-glucoside)

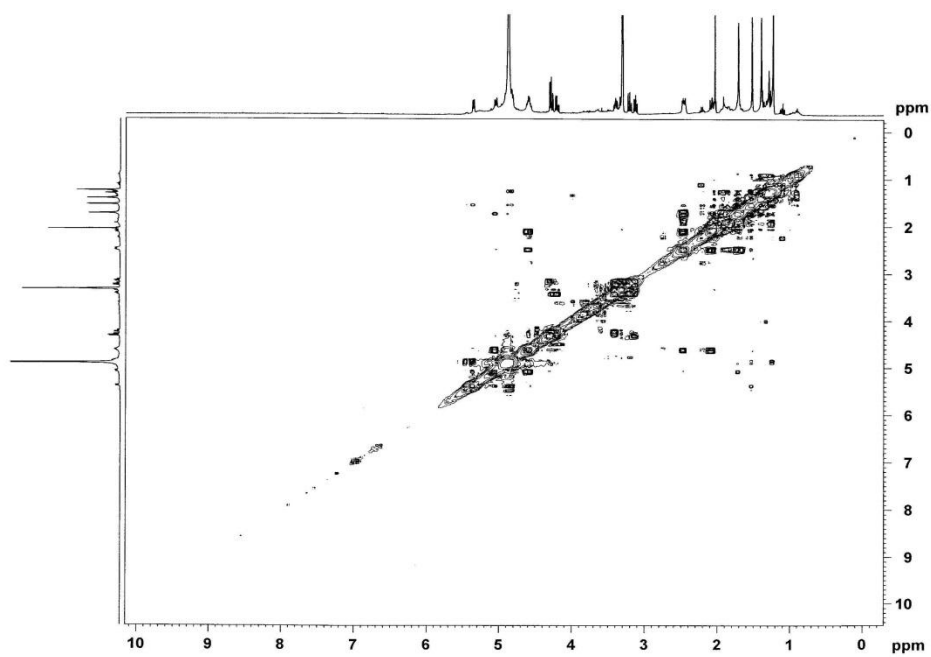
Germacradiene-6-O-(6'-O-acetyl)- β -D-glucoside (1): White amorphous powder. UV (λ_{max} , CHCl_3 , nm): 275, 241. IR (ν_{max} cm^{-1}): 3338 (-OH), 1731 (C=O). $^1\text{H-NMR}$ (CD_3OD , 400 MHz), δ : 1.23 (3H, s, H-12), 1.23 (1H, m, H-7), 1.39 (3H, s, H-13), 1.52 (3H, s, H-15), 1.70 (1H, m, H-9b), 1.71 (1H, m, H-8b), 1.71 (3H, s, H-14), 2.03 (3H, s, OCOCH_3), 2.03 (1H, m, H-8a), 2.10 (1H, m, H-3b), 2.47 (1H, dd, H-3a), 2.47 (1H, m, H-9a), 3.13 (1H, t, H-2'), 3.21 (1H, t, H-4'), 3.33 (1H, m, H-3'), 3.40 (1H, m, H-5'), 4.20 (1H, dd, H-6'b), 4.28 (1H, dd, H-6'a), 4.30 (1H, d, H-1'), 4.60 (1H, ddd, H-2), 4.82 (1H, d, H-6), 5.05 (1H, d, H-1), 5.36 (1H, d, H-5). $^{13}\text{C-NMR}$ (CD_3OD , 100 MHz), δ : 132.6 (C-1), 66.0 (C-2), 48.0 (C-3), 130.1 (C-4), 134.4 (C-5), 80.4 (C-6), 50.0 (C-7), 25.8 (C-8), 35.6 (C-9), 136.2 (C-10), 73.3 (C-11), 27.1 (C-12), 28.3 (C-13), 21.3 (C-14), 16.2 (C-15), 103.7 (C-1'), 73.7 (C-2'), 76.8 (C-3'), 70.4 (C-4'), 74.0 (C-5'), 63.4 (C-6'), 171.2 (C=O), 19.4 (OCH_3). HR-ESI-MS: m/z 481.2429 (calc. for $\text{C}_{23}\text{H}_{38}\text{O}_9\text{Na}$).



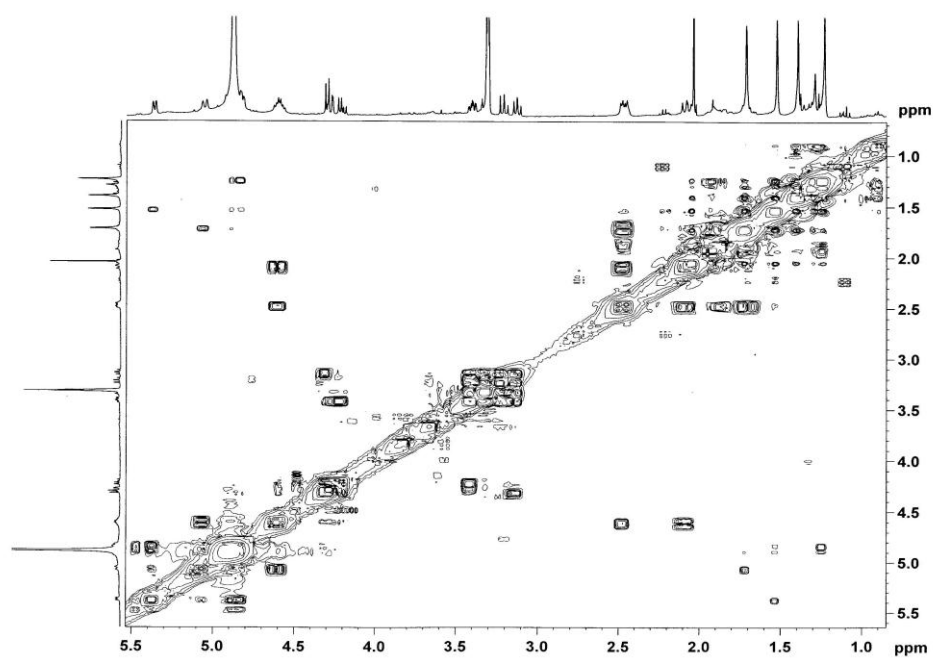
S3: ¹³C-NMR (100 MHz, CD₃OD) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)-β-D-glucoside)



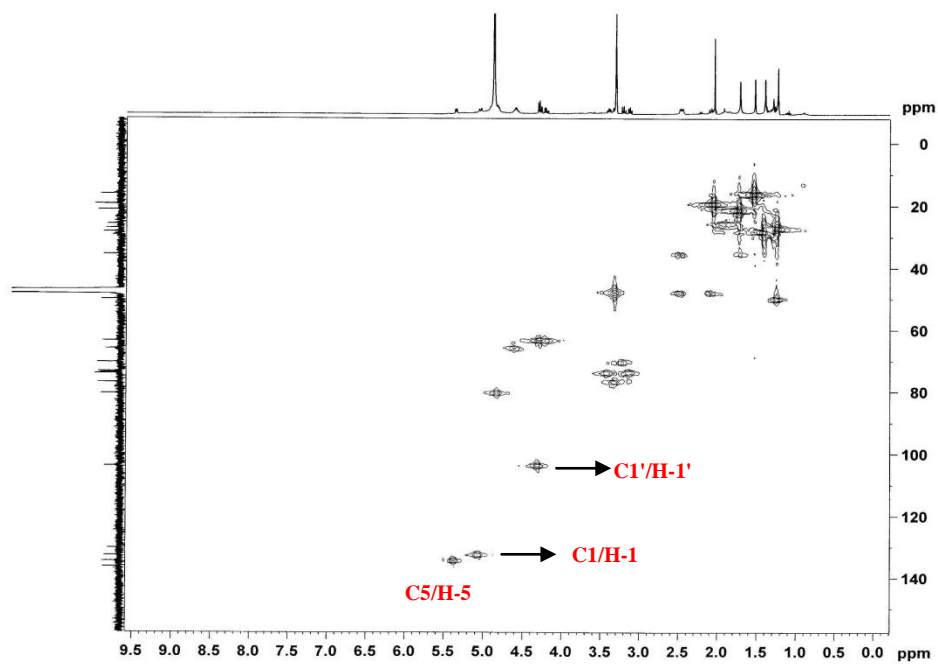
S4: DEPT (100 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)



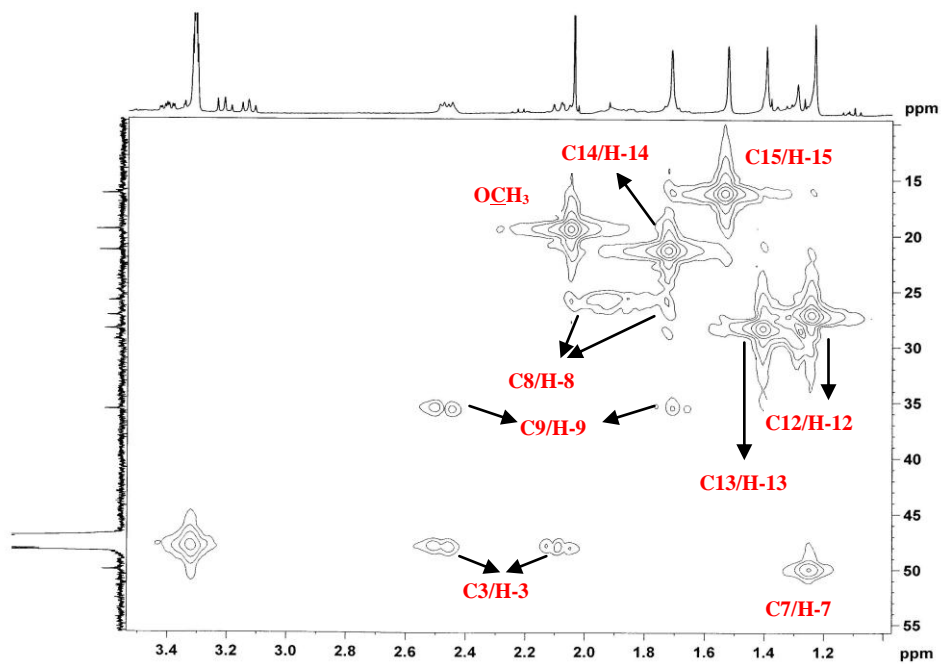
S5: COSY (400 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)



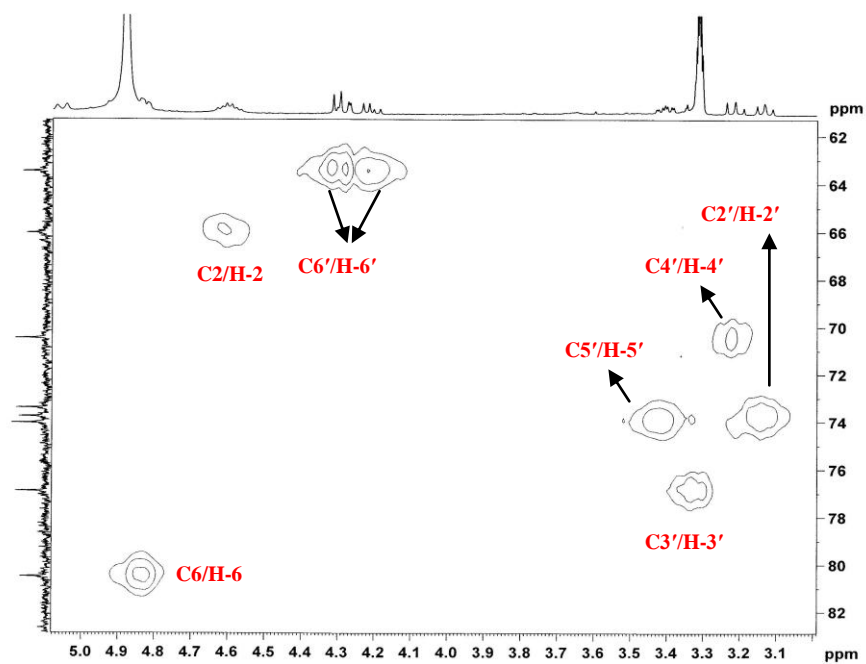
S6: COSY Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)
(From 1.0 to 5.5 ppm)



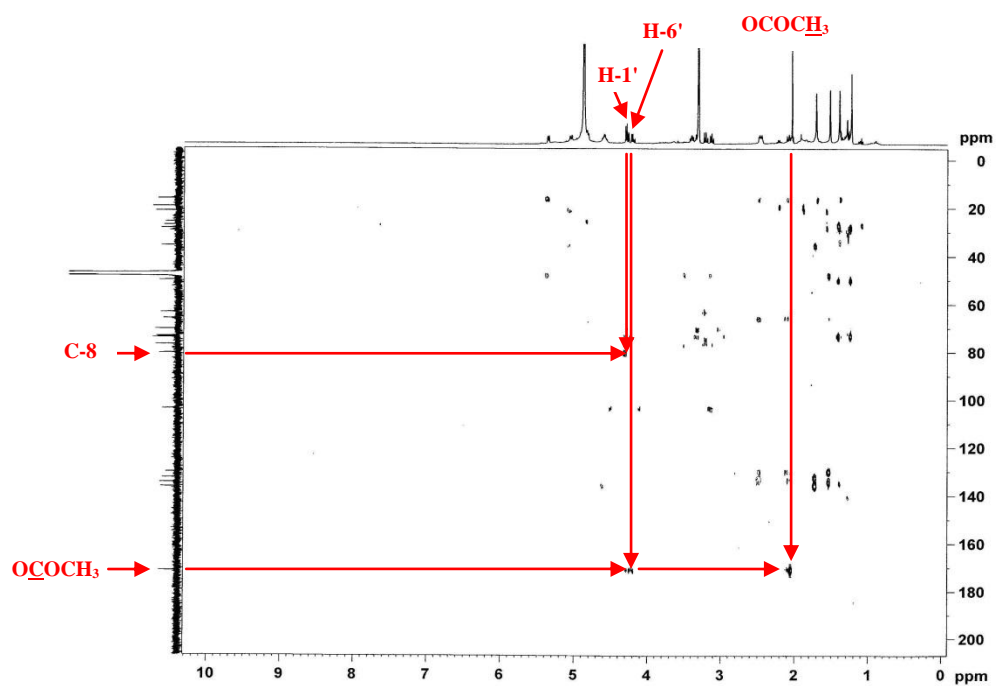
S7: HMQC (400 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)



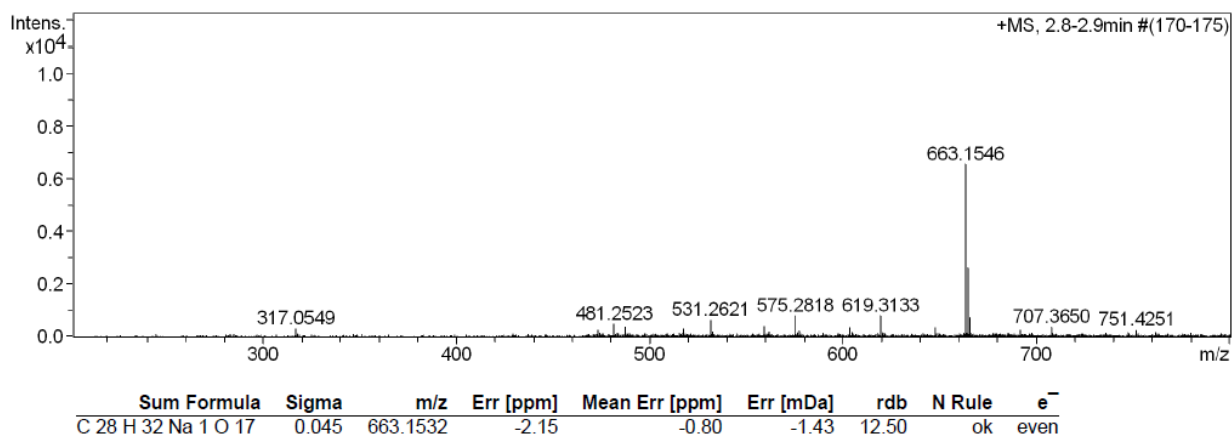
S8: HMQC (400 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside) (From 10 to 55 ppm)



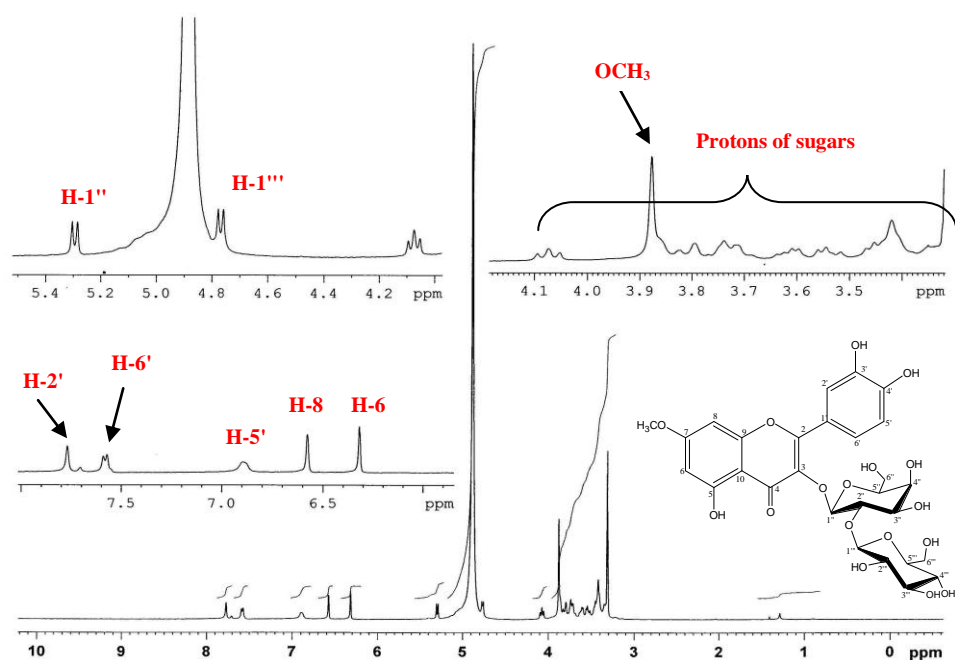
S9: HMQC (400 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside) (From 60 to 85 ppm)



S10: HMBC (400 MHz) Spectrum of Compound **1** (Germacradiene-6-*O*-(6'-*O*-acetyl)- β -D-glucoside)

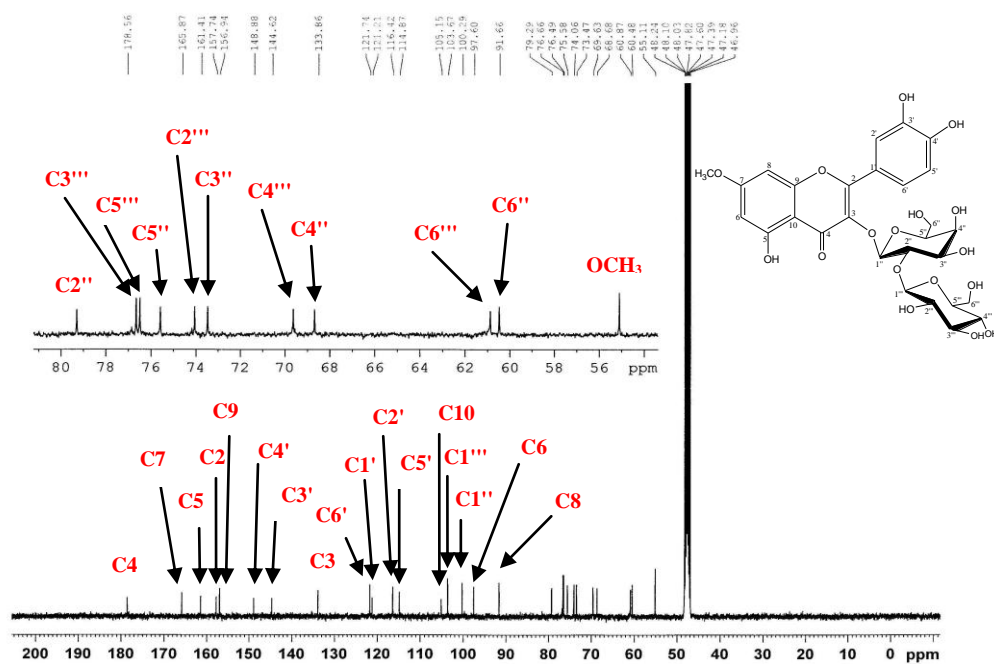


S11: HR-ESI-MS Spectrum of Compound **2** (Rhamnetin-3-*O*-(2''-*O*- β -D-glucopyranosyl)- β -D-galactopyranoside)

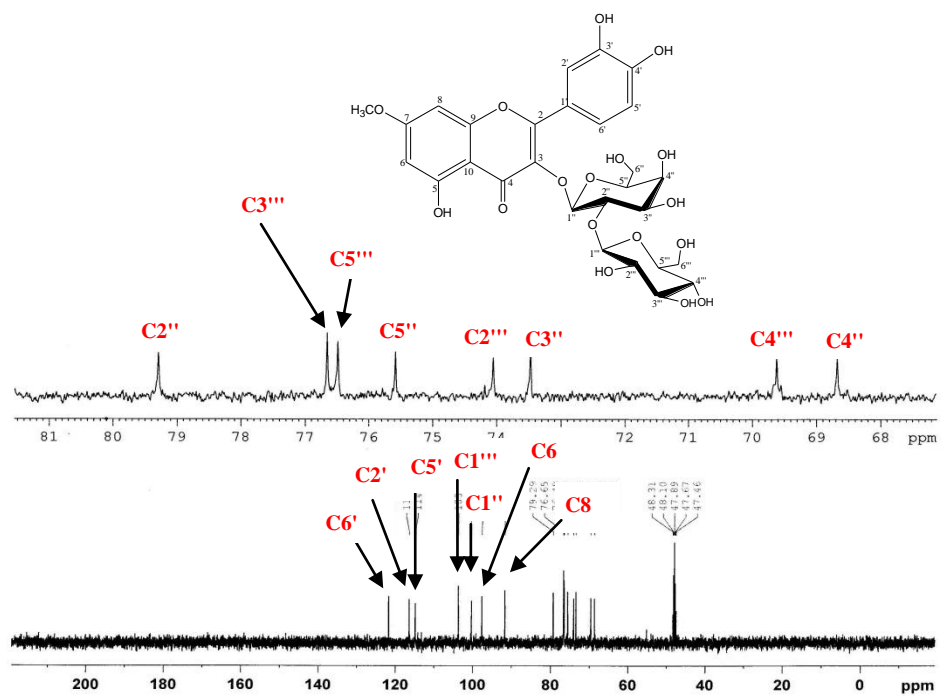


S12: $^1\text{H-NMR}$ (400 MHz, CD_3OD) Spectrum of Compound **2** (Rhamnetin-3-*O*-(2''-*O*- β -D-glucopyranosyl)- β -D-galactopyranoside)

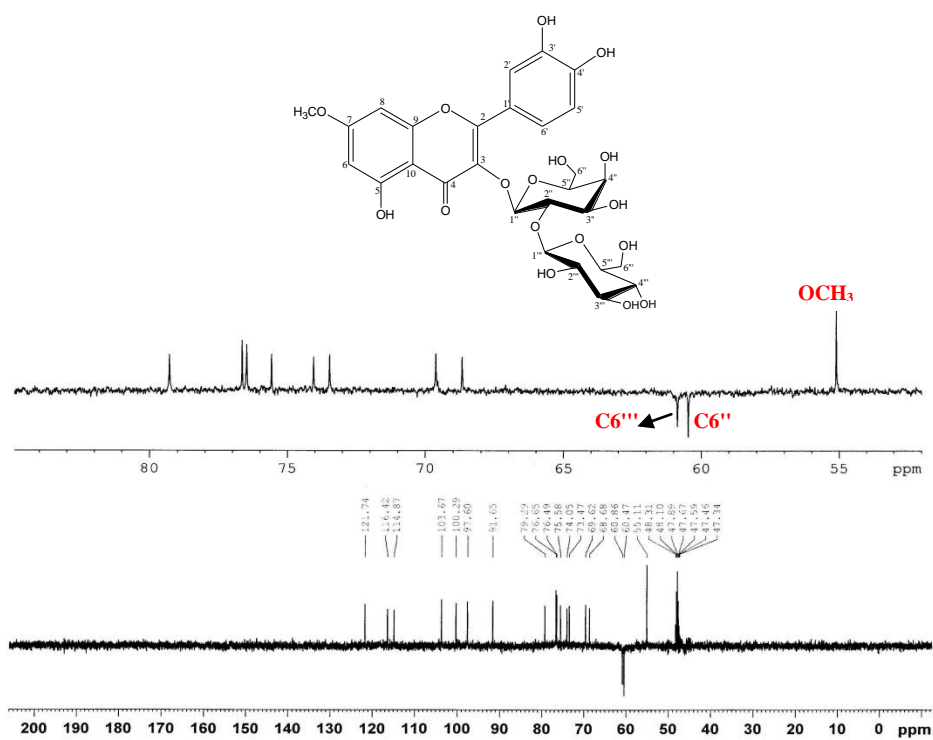
Rhamnetin-3-O-(2''-O- β -D-glucopyranosyl)- β -D-galactopyranoside (2): Yellow amorphous powder, UV (λ_{max} , MeOH, nm): 357, 256. IR (ν_{max} cm^{-1}): 3301 (-OH), 1651 (C=O), 1592 (C=C). $^1\text{H-NMR}$ (CD_3OD , 400 MHz), δ : 3.33 (1H, m, H-3'''), 3.43 (1H, m, H-2'''), 3.44 (1H, m, H-4'''), 3.45 (1H, m, H-5'''), 3.46 (1H, m, H-5''), 3.53 (1H, dd, H-6''b), 3.61 (1H, dd, H-6''a), 3.72 (1H, m, H-6'''b), 3.73 (1H, m, H-3''), 3.79 (1H, m, H-6'''a), 3.87 (1H, m, H-4''), 3.87 (3H, s, OCH₃), 4.07 (1H, t, H-2''), 4.76 (1H, d, H-1'''), 5.29 (1H, d, H-1''), 6.31 (1H, bs, H-6), 6.57 (1H, bs, H-8), 6.89 (1H, d, H-5'), 7.58 (1H, dd, H-6'), 7.77 (1H, d, H-2'). $^{13}\text{C-NMR}$ (CD_3OD , 100 MHz), δ : 157.7 (C-2), 133.8 (C-3), 178.5 (C-4), 161.4 (C-5), 97.6 (C-6), 165.8 (C-7), 91.6 (C-8), 156.9 (C-9), 105.1 (C-10), 121.2 (C-1'), 116.4 (C-2'), 144.6 (C-3'), 148.8 (C-4'), 114.8 (C-5'), 121.7 (C-6'), 55.1 (O-CH₃), 100.2 (C-1''), 79.2 (C-2''), 73.4 (C-3''), 68.6 (C-4''), 75.5 (C-5''), 60.4 (C-6''), 103.6 (C-1'''), 74.0 (C-2'''), 76.6 (C-3'''), 69.6 (C-4'''), 76.4 (C-5'''), 60.8 (C-6'''). HR-ESI-MS: m/z 663.1546 (calc. for $\text{C}_{28}\text{H}_{32}\text{O}_{17}\text{Na}$).



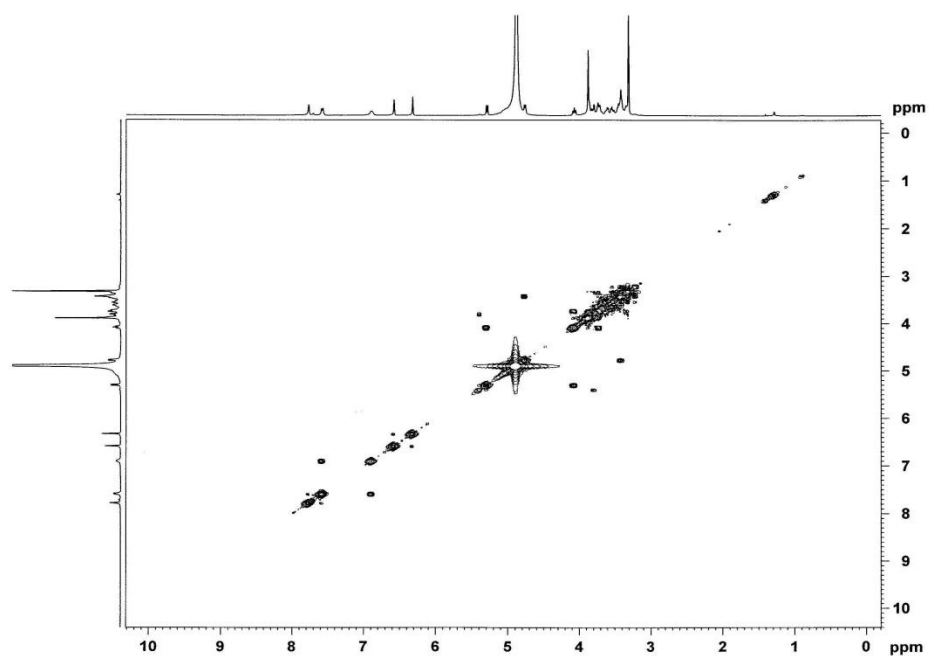
S13: ¹³C-NMR (100 MHz, CD₃OD) Spectrum of Compound 2 (Rhamnetin-3-O-(2''-O-β-D-glucopyranosyl)-β-D-galactopyranoside)



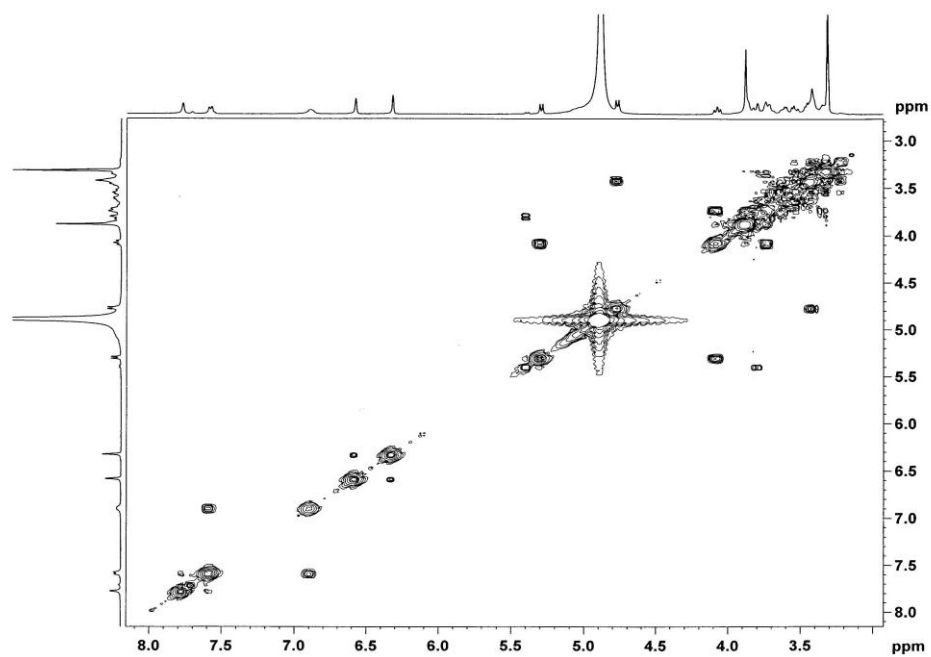
S14: DEPT 90 (100 MHz, CD₃OD) Spectrum of Compound 2 (Rhamnetin-3-*O*-(2''-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside)



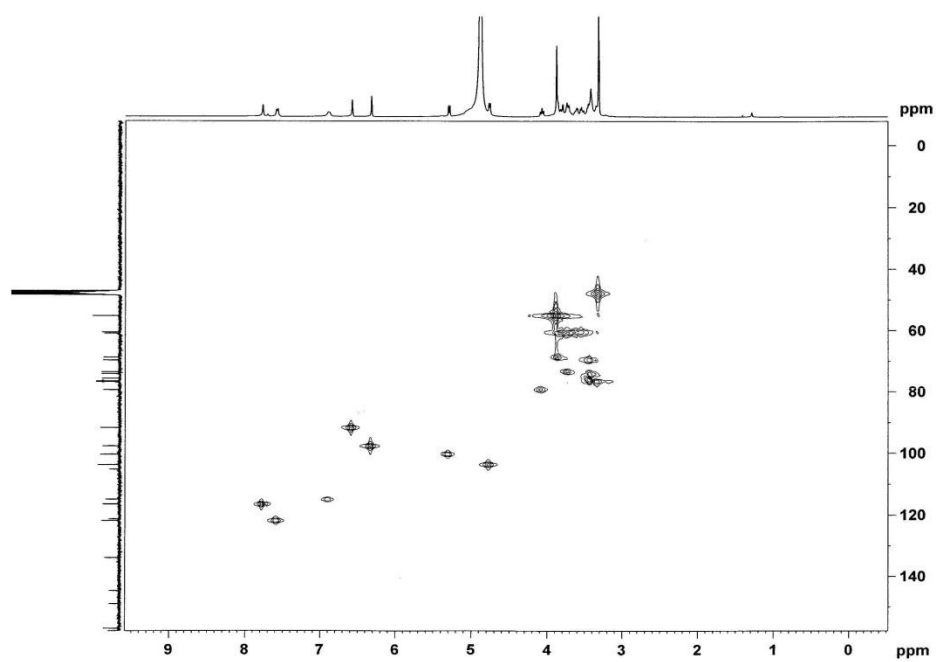
S15: DEPT 135 (100 MHz, CD₃OD) Spectrum of Compound 2 (Rhamnetin-3-*O*-(2''-*O*-β-D-glucopyranosyl)-β-D-galactopyranoside)



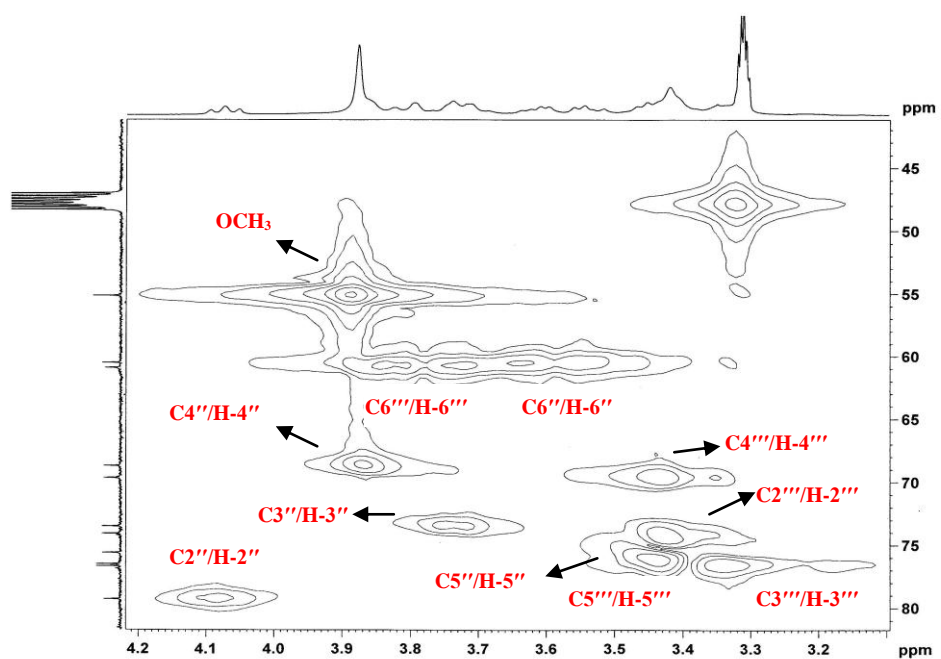
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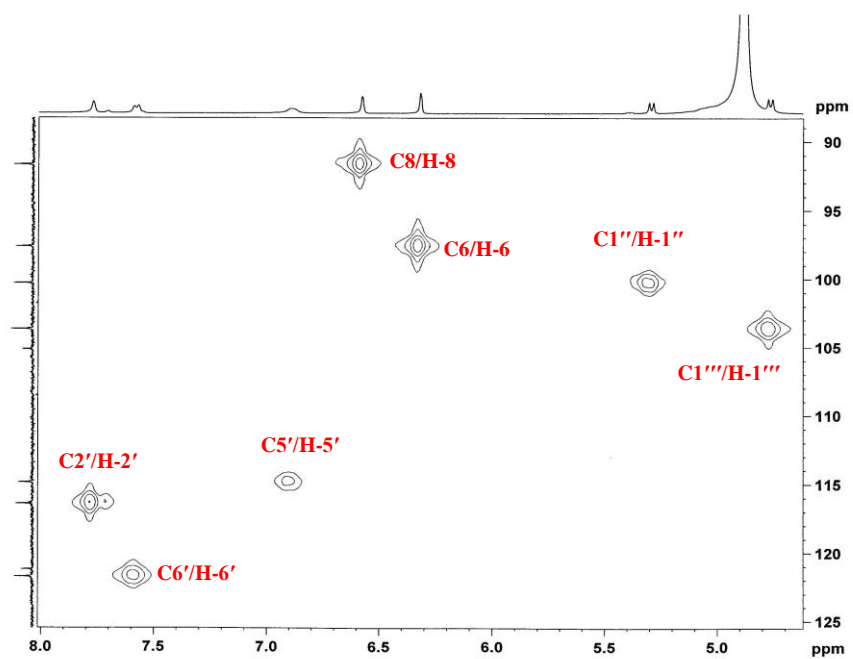
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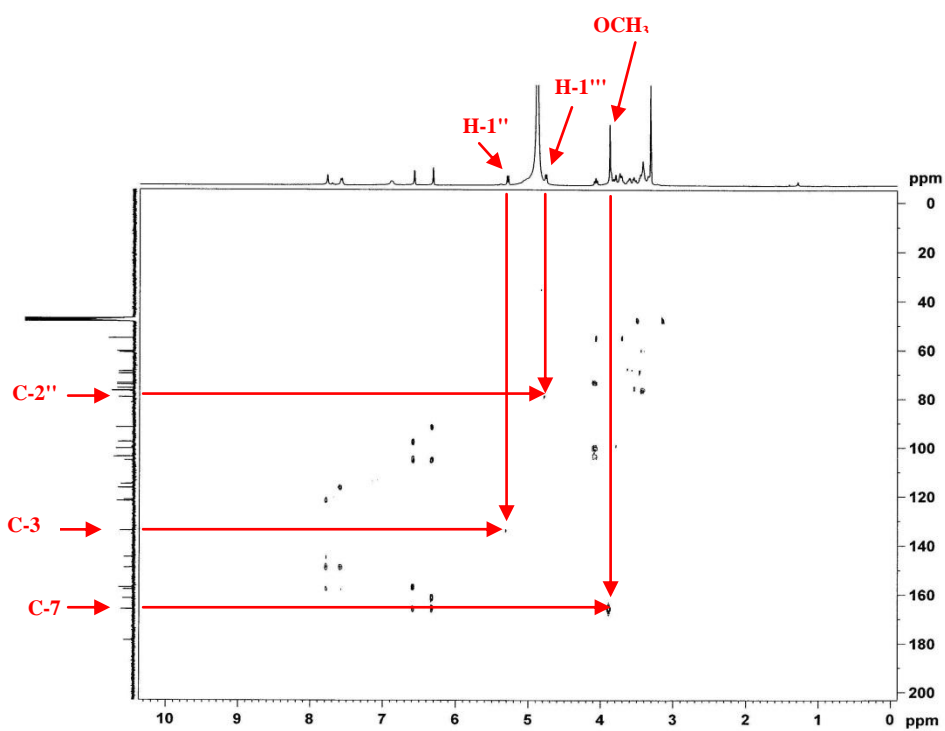
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S19: HMQC (400 MHz) Spectrum of Compound **2** (Rhamnetin-3-*O*-(2''-*O*- β -D-glucopyranosyl)- β -D-galactopyranoside) (From 40 to 80 ppm)



S20: HMQC (400 MHz) Spectrum of Compound **2** (Rhamnetin-3-*O*-(2''-*O*- β -D-glucopyranosyl)- β -D-galactopyranoside) (From 90 to 125 ppm)



S21: HMBC (400 MHz) Spectrum of Compound **2** (Rhamnetin-3-*O*-(2''-*O*- β -D-glucopyranosyl)- β -D-galactopyranoside)